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Catalytic Ignition of Ionic Liquid Fuels by Ionic Liquids

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14. ABSTRACT
The majority of current hypergolic ionic liquids (ILs) are hypergolic (spontaneous ignition upon contact between a fuel and oxidizer) with nitric acid in one of its several formulations. Only very few have been found to be hypergolic with higher performing N_2O_4. While ILs can be considered "green" or less hazardous in certain aspects when compared to hydrazine, both nitric acid and N_2O_4 are highly hazardous. To gain a true advantage, a more environmentally friendly oxidizer must be considered. Hydrogen peroxide might be an attractive alternative for some systems, especially because of its benign decomposition products. Although the permissible exposure limit for hydrogen peroxide is only 1 ppm in air, the high boiling points of its water solutions, 141°C (90% hydrogen peroxide) and 148°C (98% hydrogen peroxide), result in relatively low vapor pressures at 25°C of only 0.5 KPa and 0.3 KPa, respectively. In 2011, we showed that ILs can be hypergolic with H_2O_2 but it required complex aluminumborohydride anions to realize acceptable ignition delay (ID) times.[1] Here we describe how certain ILs can be employed as ignition enhancing catalyst to make many ILs hypergolic.

15. SUBJECT TERMS

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a. REPORT	b. ABSTRACT	c. THIS PAGE			Stefan Schneider
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Catalytic Ignition of Ionic Liquid Fuels by Ionic Liquids

ACS San Francisco 2014

A. Beauchamp
Edwards AFB, CA

Where are we located?

- **70 miles North-East of Los Angeles**

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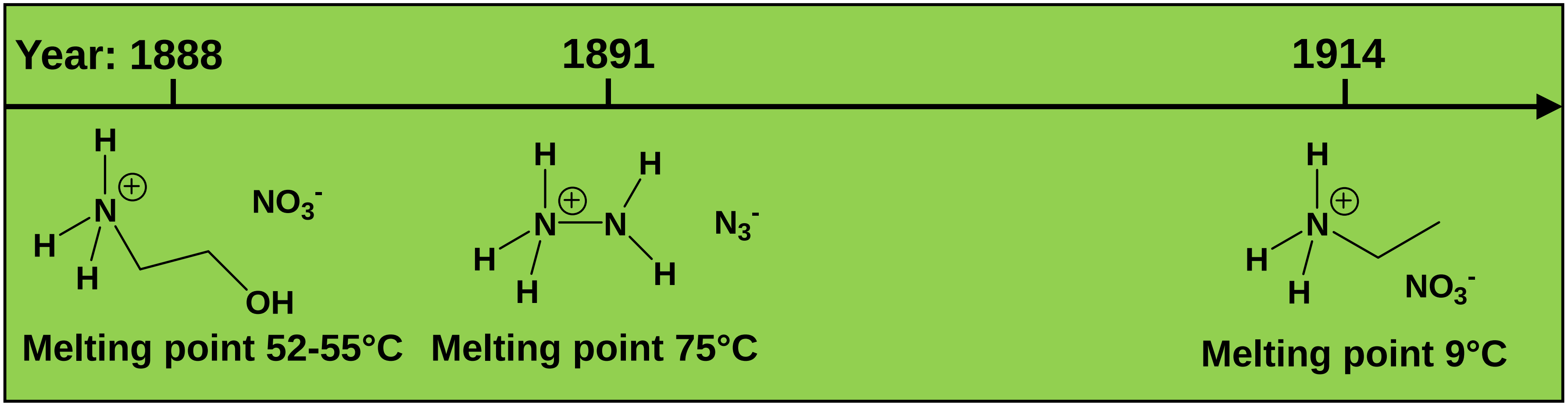
Timeline of Energetic Ionic Liquids



Gabriel, S. *Berichte,* **1888**, *21*, 2664.Curtius, T. *Ber. Dtsch. Chem. Ges.* **1891**, *24*, 3341. Walden, P. *Bull. Acad. Imp. Sci,* **1914**, 1800.

“Molten salts are nothing new, but these were the only ones I ever heard of that were liquid at 25°C. I’ve never found a use for the ethylamine compound, but something with such interesting properties ought to be good for *something!*”

John D. Clark, Ignition! An Informal History of Liquid Rocket Propellants, Rutgers University Press, New Brunswick, New Jersey, 1972

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Why ILs as Energetic Materials?

<u>"Tuning" IL structure for</u>:
Energy content
Oxygen balance
Melting point
Liquid range
Ignition behavior

<u>Propulsion</u>:
Thrusters

<u>Explosives</u>:
Melt-cast munitions

<u>?????</u>
Power generators, APUs,….

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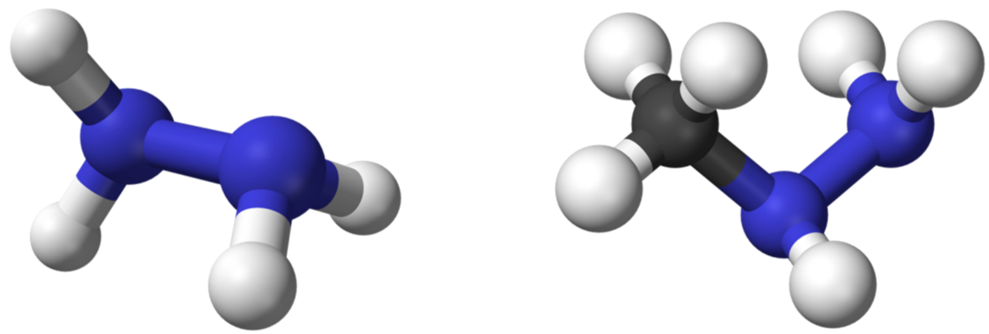
Hydrazine – A State of the Art Rocket Fuel

Hydrazine	Monomethylhydrazine



- **Hydrazine fuel vapor toxicity can increase testing/operations costs:**
  - **System Handling/Fueling by certified crews in high level PPE**
  - **Monitoring system in field**
- **Vapor toxicity can limit transportation options**

Ionic Liquid fuels can eliminate vapor toxicity and possess acceptable safety properties

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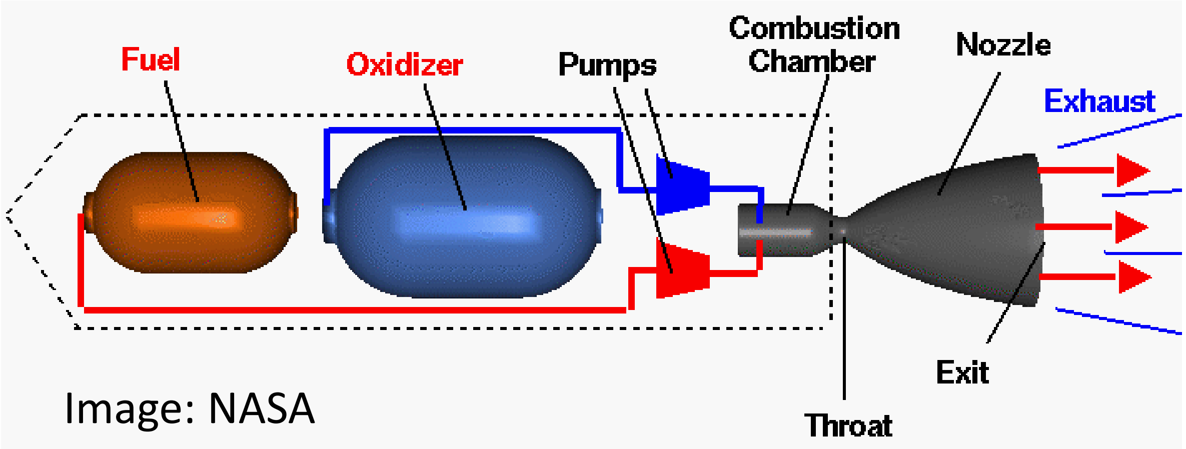
Objectives for Ionic Liquids as Bipropellant Fuels



- ❑ Ignites (Hypergolic)
- ❑ Ignites Fast (<10ms)
- ❑ Ignites Fast & Green(er)

Prospect for Hypergolicity – Driving Force Behind IL Azides

- **Simple ionic azides such as Me_4NN_3 and NaN_3 form nitrates in N_2O_4.**
- **The reaction involves the unstable intermediate NON_3 which completely decomposes to N_2 and N_2O.**

$$N_2O_4 \rightleftarrows NO_3^- + NO^+$$

$$N_3^- + NO^+ \rightleftarrows N_3NO \longrightarrow N_2 + N_2O$$

$$\overline{N_2O_4 + N_3^- \longrightarrow NO_3^- + N_2 + N_2O}$$

- **If this reactions is "hot" enough it could lead to hypergolic ignition.**

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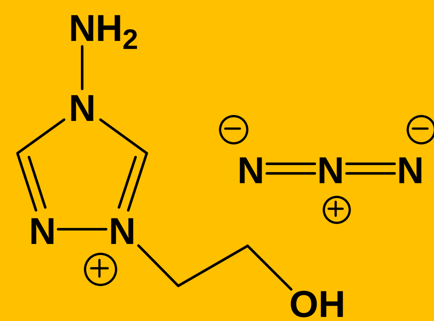
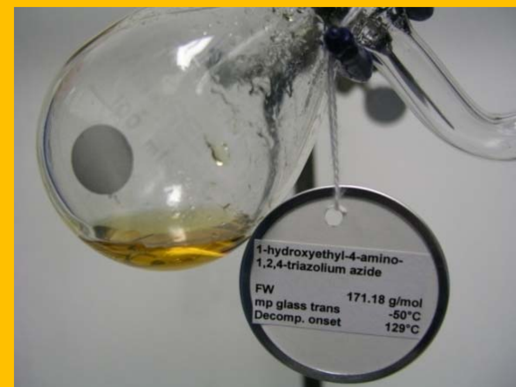
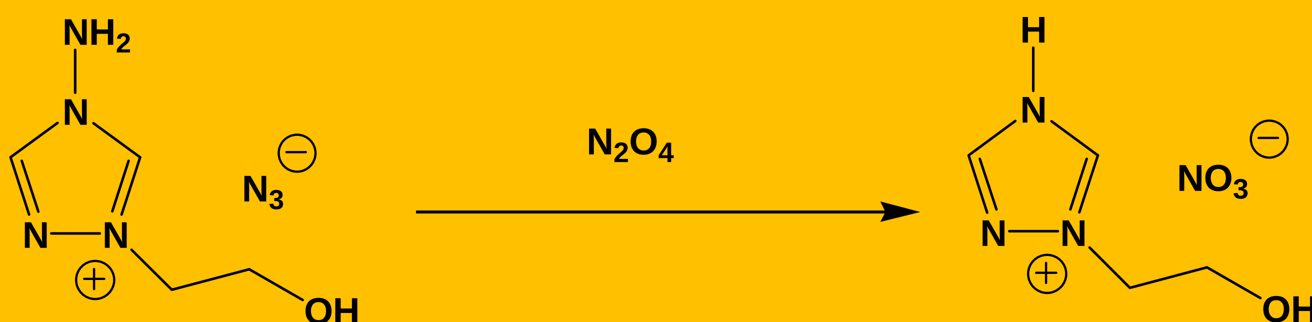
Thermal Stability and Reactivity of IL Azides

- NOT ***HYPERGOLIC*** with WFNA, RFNA, IRFNA, NTO or H_2O_2





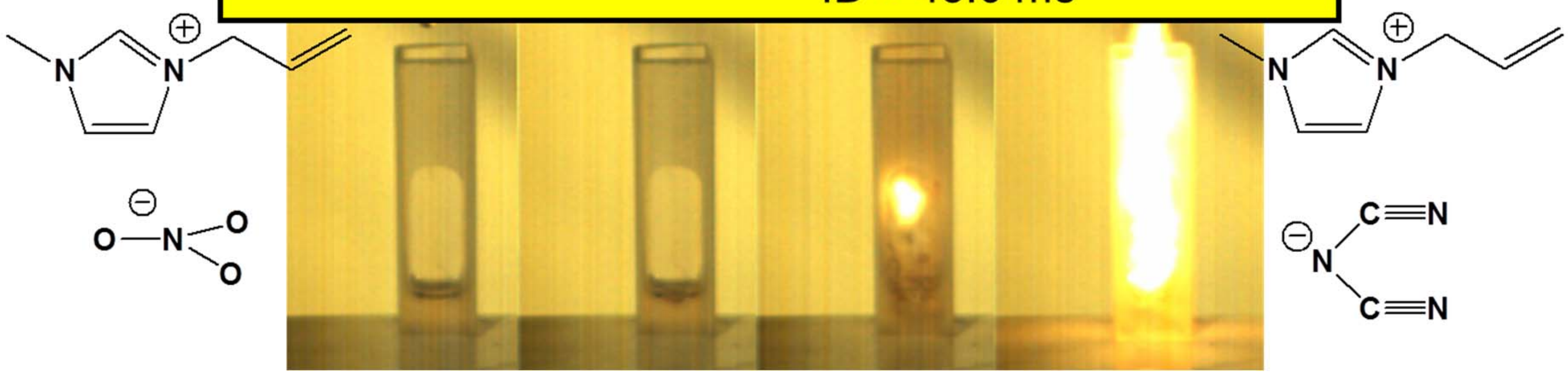


- **Decomp onset of 129°C indicated marginal stability**
- **TGA mass loss > 12% isothermal for 48 h @ 75°C**

Schneider, S.; Hawkins, T.; Rosander, M.; Mills, J.; Vaghjiani, G.; Chambreau, S. *Inorg. Chem.* **2008**, 47(13), 6082-6089.

Anion Control of Hypergolic Activity

Oxygenated	**Fuel-Rich**
Oxidizer: White fuming nitric acid	
Not Hypergolic	***Hypergolic***; ID ≈ 43.0 ms



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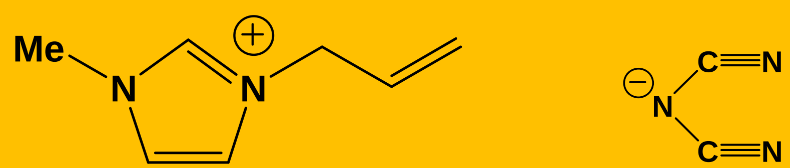
Search for Trigger Group – Faster Ignition

Oxidizer: WFNA	Ignition Delay [ms]
	47
	43
	15

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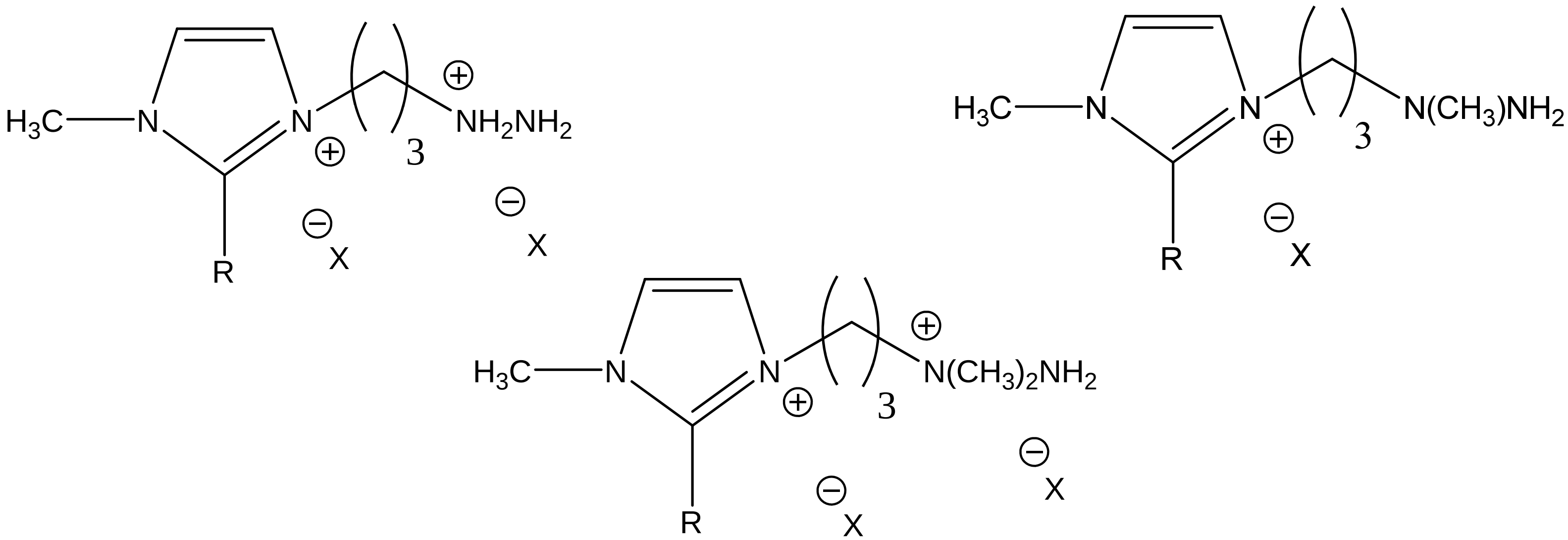
Cation Control of Hypergolic Activity



- **Focus on development of cationic structures, which allow for fast, hypergolic ignition with common oxidizers independent of the accompanying anion.**
- **The ability to endow the cation with a hypergolic “trigger” widens the synthetic design space available for hypergolic fuels and provides another possible avenue for the promotion of rapid ignition.**

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Requirements for a “Green(er)” Oxidizer

- ❑ **Storable! (non cryogenic)**
- ❑ **High performing!**

Desirable –

- ❑ **Can be served as a refreshing drink ☺**

What's Out There?

- **WATER!**
- **Nitric Acid (extreme corrosivity)**
- **N_2O_4 (less corrosive, high toxicity combined with high vapor pressure)**
- **H_2O_2 (less toxic vapor and corrosivity, environmental benign decomposition products)**

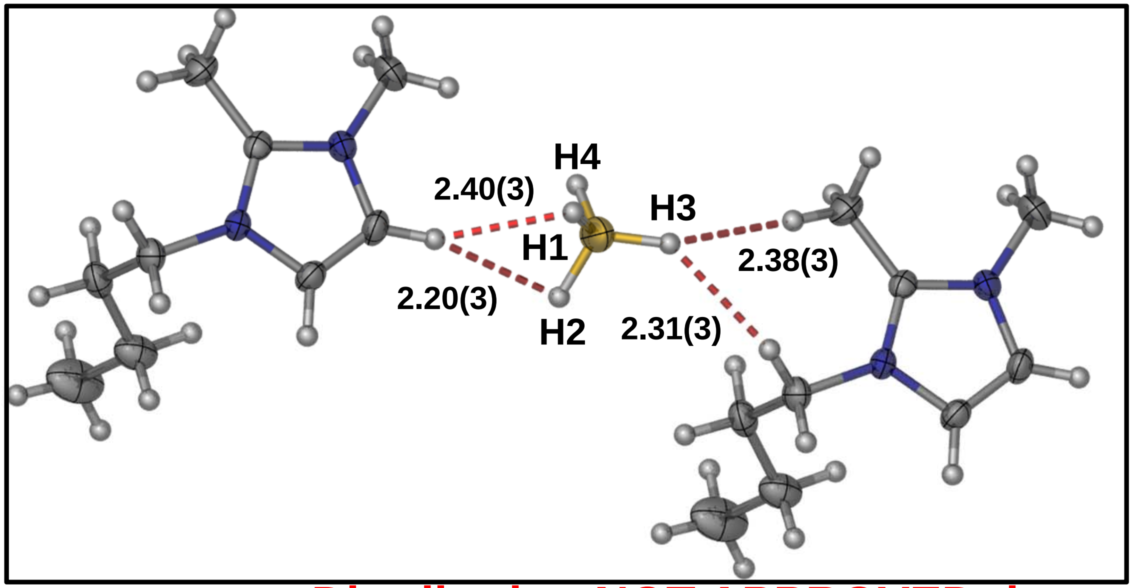
Lack of heterocyclic BH_4 salts

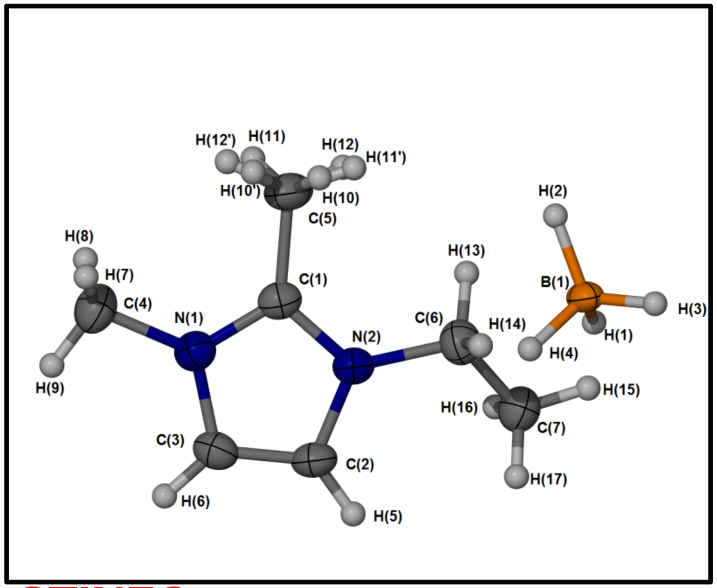
- **Published routes to BMIM BH_4 used IL halide in acetonitrile or CH_2Cl_2**
- **This work could not be reproduced and only yielded material with substantial halide content**

  Best results 77.5% $[BH_4]^-$ halide content 22.5%

  M. Bürchner, A.M.T. Erle, H. Scherer, I. Krossing *Chem. Eur. J.* **2012**, *18*, 2254.

- **Heterocyclic borohydride salts tend to have undesirable physical properties**





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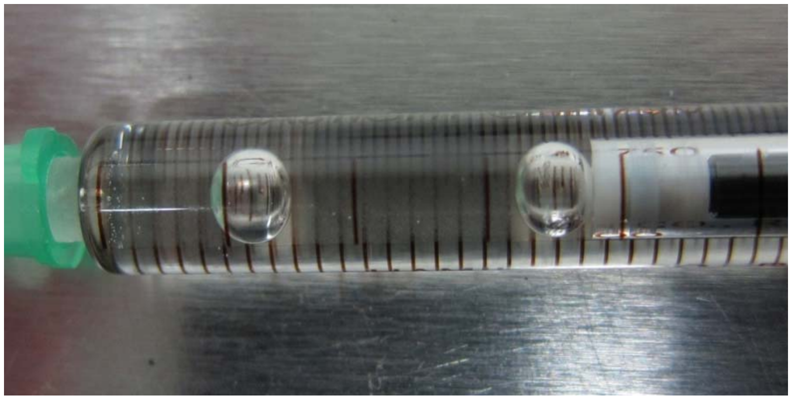
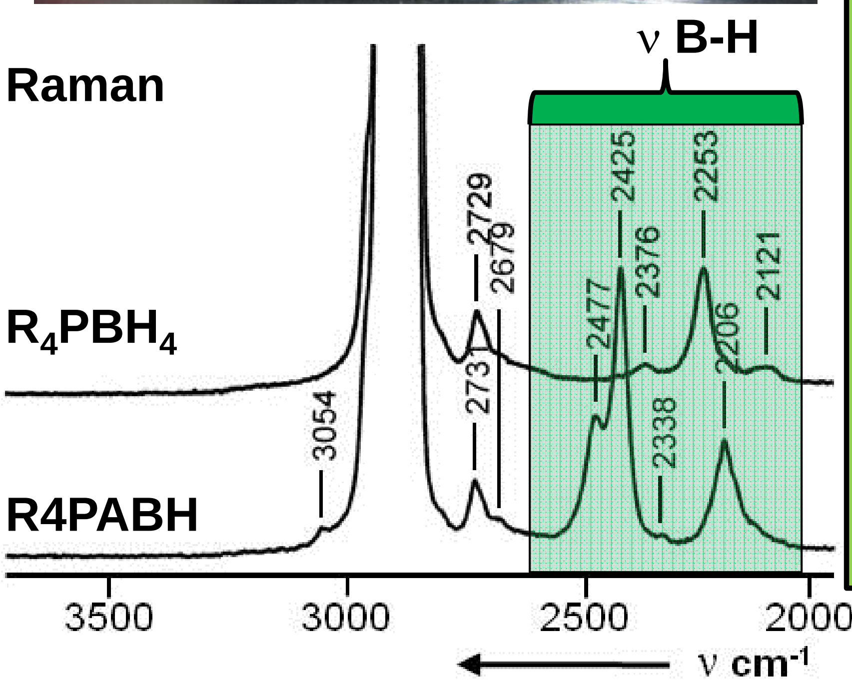
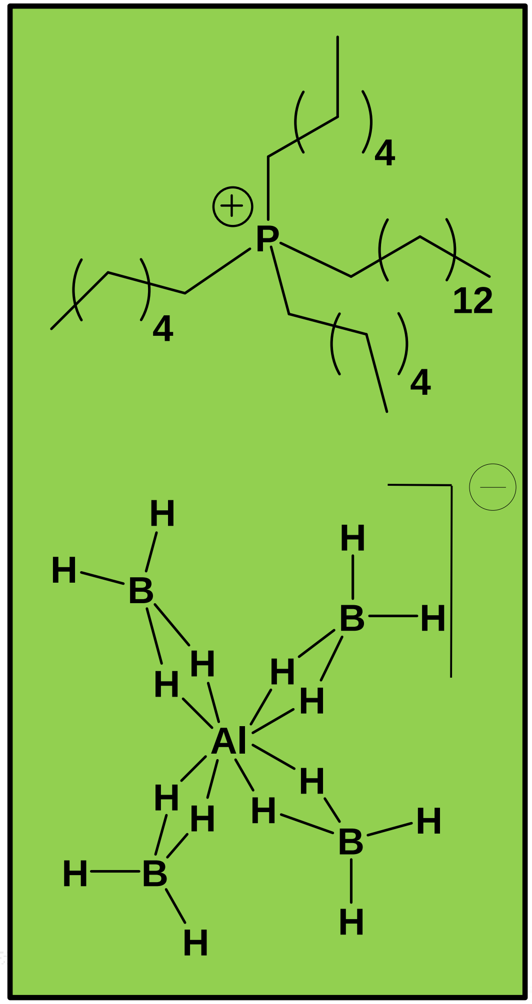
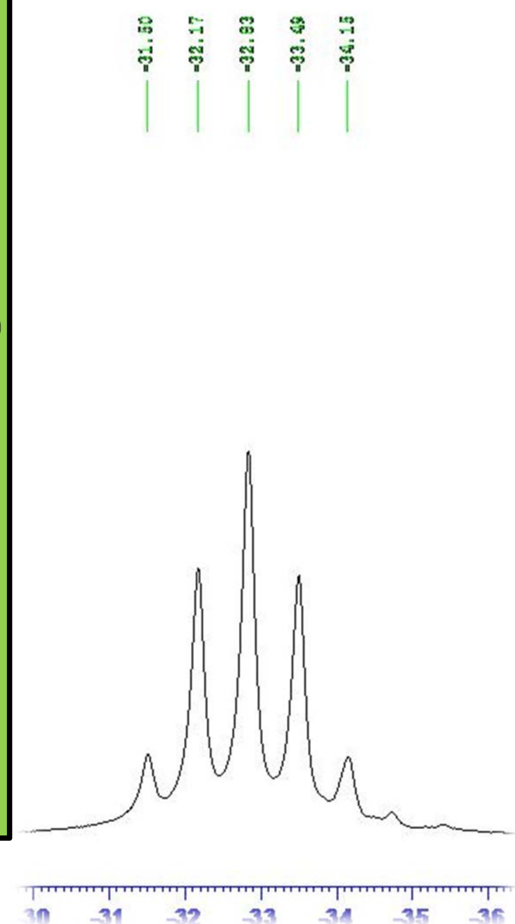
Trihexyltetradecylphosphonium tetrakis(tetrahydroborato)aluminate







^{11}B NMR of R_4PABH



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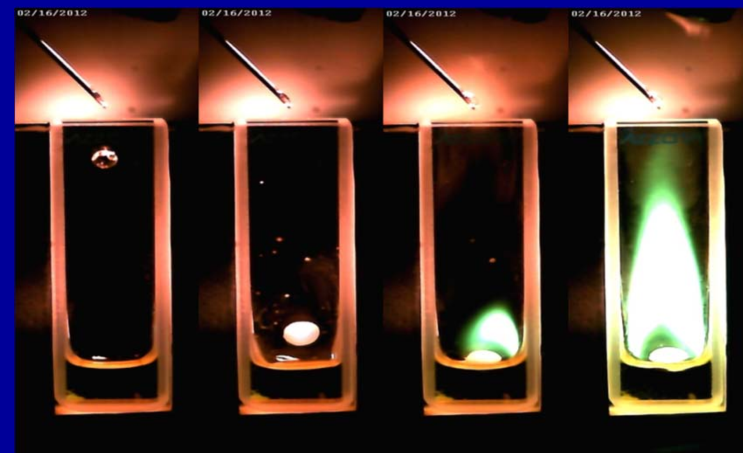
Response Times of CBH ILs towards Nitric acid and Hydrogen peroxide

Compound	ID (ms) with HNO_3	ID (ms) with 90% H_2O_2
	5	332/384/>1s
	11	>3s
	600	>3s
	901[2]	808



- In the case of the ethylammonium salt, the drop surface of the fuel was so quickly oxidized that the fuel became momentarily immiscible with the oxidizer.

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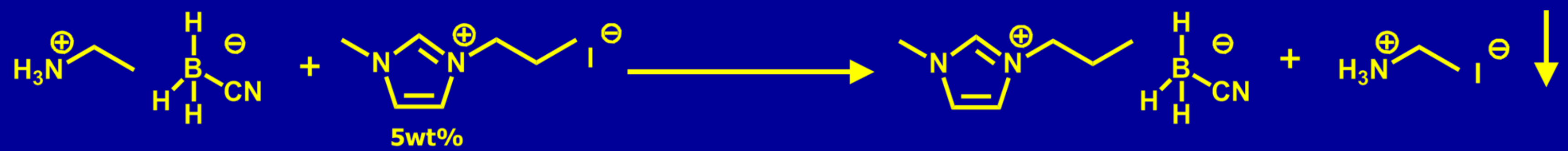
Catalytic approach for H_2O_2 decomposition

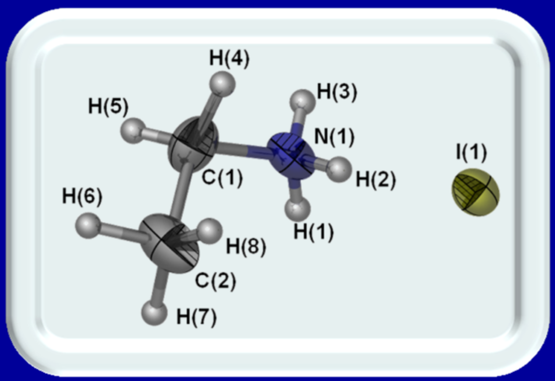
- Many transition-metal salts of Fe^{+2}, Fe^{+3}, Co^{+2}, Co^{+3}, Ni^{+1}, Ni^{+2}, Cu^{+1}, Cu^{+2}, Mn^{+2} and V^{+2} as well as NaI have been used to accelerate the decomposition of hydrogen peroxide.
- Ultimately this led to hypergolic ignition between a catalyst-loaded fuel and hydrogen peroxide.
- Typical problems encountered were either a reaction between the metal salt and the fuel or precipitation.
- Also, the metal ions are not catalysts in the classical sense, but are reacting with hydrogen peroxide.
- The iodide anion on the other hand is known to catalytically decompose hydrogen peroxide.

$$H_2O_2 + I^- \longrightarrow IO^- + H_2O$$
$$H_2O_2 + IO^- \longrightarrow I^- + H_2O + O_2$$
$$\overline{}$$
$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

Multi ion systems

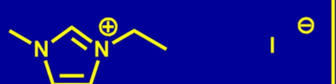
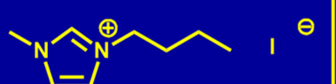
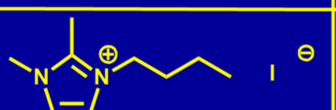
- ❑ Substituting Na for an organic ammonium cation increases the overall energy content and hopefully the solubility of the iodide salt in the fuel.
- ❑ In the case of multiple cation systems, metathesis reactions can easily take place.





Ionic Liquid iodides in cyanoborohydride

- **No precipitation of the ethylammonium iodide salts was observed even after several months of ambient storage.**

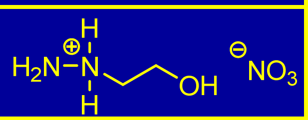
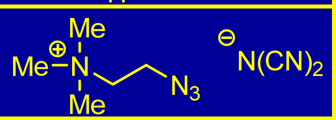
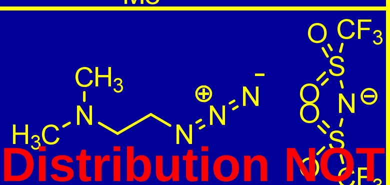
Compound	Melting point
	80°C
	(glass)-29°
	99°C
	54°C

Compound	ID (ms) with 90% H_2O_2 1wt% I^-	5wt% I^-	10wt% I^-	Catalyst
	208/440	47/49		
		116/119		
		118/124		
	275/372	47/56	30/31	

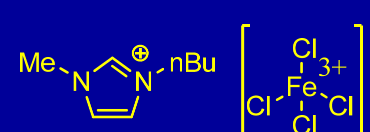
Catalytic Ignition in H_2O_2

- **97% H_2O_2 used as oxidizer**
- **No ignition with catalyst 'neat'**

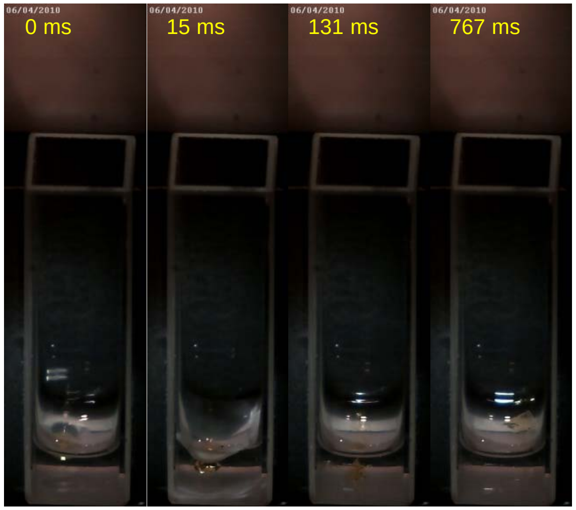
ID (ms) with 97% H_2O_2

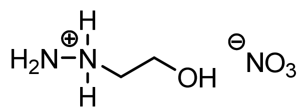
Compound	18 Wt% Catalyst	16 Wt% Catalyst	8 Wt% Catalyst	0 Wt% Catalyst
	50			No Ignition
			130	No Ignition
		875		No Ignition

Catalyst

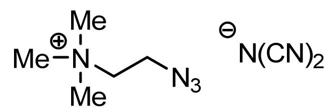


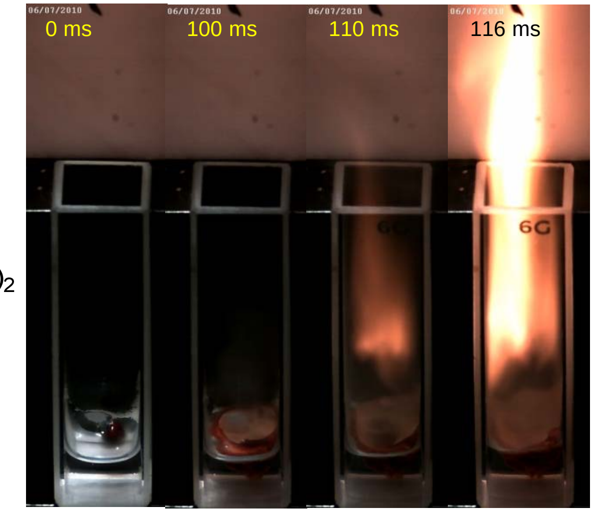
Catalytic Hypergolic Ignition



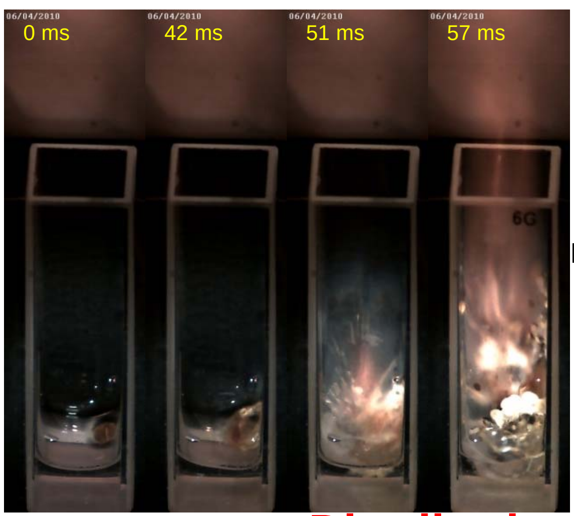


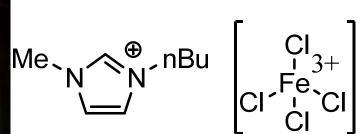
• HEHN





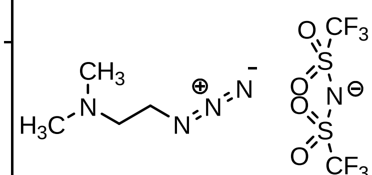
• TMAZDCA with Catalyst

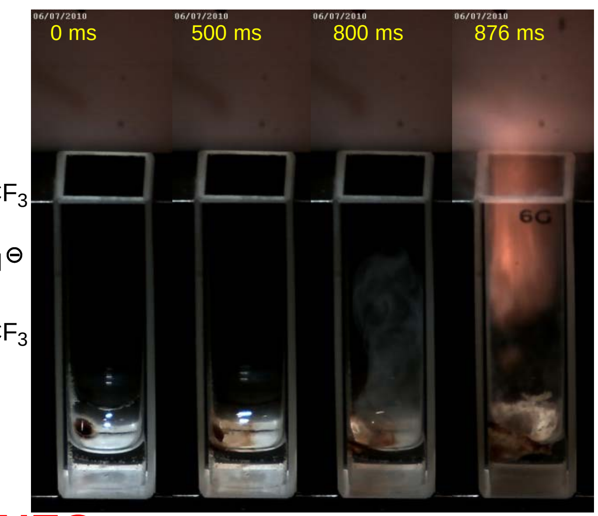




Catalyst BMIM $FeCl_4$

• HEHN with Catalyst





• DMAZTF with Catalyst

Summary and Conclusion

- Continuing to synthesize new fuel candidates with hypergolic triggers and desirable physical properties
- Pairing new fuel candidates with green(er) oxidizers
- Established storable fuel/catalyst IL mixtures
- First demonstration of ignition of non-hypergolic ILs utilizing IL catalysts in H_2O_2

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